

Polymetallic complexes: Part XXVI— Complexes of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II) with chelating bis-bidentate ON NO donor bases

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Schiff bases synthesized by the reaction of benzoinhydrazone with salicylaldehyde and *o*-hydroxyacetophenone form dimeric complexes with divalent metal ions. An octahedral geometry has been assigned to the complexes of Co(II), Ni(II), Cu(II) and Zn(II) whereas a tetrahedral structure is suggested for the Cd(II) and Hg(II) complexes. The complexes are amorphous, have high melting points and are insoluble in common organic solvents. The complexes have been characterised on the basis of analytical, conductance, magnetic susceptibility, molecular weight, IR and electronic spectral data.

In continuation of our earlier reports on the preparation of polymetallic complexes using bis-bidentate ligands¹⁻⁴, the present note reports the synthesis of two new schiff bases having ON NO donor atoms and their complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).

Benzoin, hydrazine hydrate, salicylaldehyde and *o*-hydroxyacetophenone were BDH reagents.

Experimental

Preparation of the schiff bases:

Benzoinhydrazone (0.01 mol) in ethanol was added separately to salicylaldehyde (0.1 mol) and *o*-hydroxyacetophenone (0.01 mol) in ethanol (15 ml) and the mixture refluxed on a water-bath for 4 hr. On keeping the solution overnight, yellow coloured schiff bases separated out. These were filtered, washed with ethanol and air-dried. Required for C₂₁H₁₈N₂O₂ (LH₂): C, 76.36; H, 5.45; N, 8.48% Found: C, 75.2; H, 5.3, N, 8.1%; Required for C₂₂H₂₀N₂O₂· (LH₂); C, 76-74; H, 5.81; N, 8.13%. Found: C, 75.8; H, 5.6; N, 8.0%. Melting points were 205°C (LH₂) and 185°C (LH₂).

The schiff bases dissolved in dioxane were mixed separately with the metal chlorides in ethanol (1:1

ratio) and the reaction mixture refluxed over a water-bath for about 0.5 hr. After cooling, conc. NH₄OH was added dropwise with stirring when the metal chelates separated out. These were filtered, washed with ethanol, ether and dried *in vacuo*.

Conductances of the complexes were measured in their 10⁻³ M DMF solutions. Magnetic moments were measured by Gouy balance at room temperature. IR spectra were recorded in KBr on a Perkin-Elmer-389 spectrophotometer. Electronic spectra were recorded in 10⁻² M DMF solutions with a Hilger and Watt uvispeck spectrophotometer. Molecular weights of the complexes were measured by the Rast method using camphor as the solvent.

Table 1—Analytical, colour and melting point data of bimetallic complexes

Compound	Colour (m.p., °C)	Found (Calc.) %	
		M	N
LH ₂	Yellow (205)	—	8.1 (8.48)
LH ₂	Yellow (185)	—	8.0 (8.13)
[Co ₂ L ₂ ·4H ₂ O]	Reddish brown (250)	13.4 (13.93)	6.5 (6.62)
[Co ₂ L' ₂ ·4H ₂ O]	Pink (250)	13.2 (13.42)	6.1 (6.37)
[Ni ₂ L ₂ ·4H ₂ O]	Yellow (250)	13.6 (13.82)	6.3 (6.59)
[Ni ₂ L' ₂ ·4H ₂ O]	Violet (250)	13.1 (13.38)	6.2 (6.38)
[Cu ₂ L ₂ ·4H ₂ O]	Brown (198)	14.4 (14.79)	6.3 (6.51)
[Cu ₂ L' ₂ ·4H ₂ O]	Green (246)	14.1 (14.32)	6.2 (6.31)
[Zn ₂ L ₂ ·4H ₂ O]	White (230 d)	14.8 (15.5)	5.9 (6.49)
[Zn ₂ L' ₂ ·4H ₂ O]	Black (250)	14.2 (14.67)	5.8 (6.28)
[Cd ₂ L ₂]	White (250)	25.1 (25.4)	6.1 (6.32)
[Cd ₂ L' ₂]	White (250)	24.3 (24.62)	5.9 (6.13)
[Hg ₂ L ₂]	White (250 d)	37.4 (37.8)	4.9 (5.27)
[Hg ₂ L' ₂]	White (250)	36.5 (36.83)	4.8 (5.14)

LH₂ = schiff base derived from benzoinhydrazone and salicylaldehyde;

LH₂' = schiff base derived from benzoinhydrazone and *o*-hydroxyacetophenone.

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Results and discussion

All the compounds are quite stable at room temperature. They do not lose mass even when heated at 100°C indicating coordinated nature of the water molecules present in Co(II), Ni(II), Cu(II) and Zn(II) complexes. The complexes have the compositions $[M_2L_2 \cdot 4H_2O]$, $[M_2L'_2 \cdot 4H_2O] \cdot [M'_2L_2]$ and $[M'_2L'_2]$ where $M = Co(II), Cu(II), Ni(II), Zn(II)$; $M' = Cd(II), Hg(II)$; $LH_2 =$ schiff base derived from benzoinhydrazone and salicylaldehyde, and $L'H_2 =$ schiff base derived from benzoinhydrazone and *o*-hydroxyacetophenone (Table 1).

In the IR spectra of the schiff bases, the band appearing at 1660 cm^{-1} (LH_2) and 1655 cm^{-1} ($L'H_2$) can be attributed to $\nu(C=N)$ vibration. The bathochromic shift of this band in the spectra of metal complexes by $\sim 10\text{ cm}^{-1}$ indicates the bonding of the imine nitrogen atom to the metal ions^{5,6}. In the ligands, the bands appearing at $\sim 2840\text{ cm}^{-1}$ can be ascribed to $\nu(OH)$ vibration, which is lowered due to $O-H \cdots N$ hydrogen bonding. Disappearance of this band in the metal complexes shows the deprotonation of the hydroxylic group thereby confirming the bonding of the oxygen atoms to the metal ions. The band at 1205 cm^{-1} (LH_2) and 1240 cm^{-1} ($L'H_2$) can be assigned to $\nu(C-O)$ (hydroxylic); in the metal complexes it is observed at ~ 1200 and $\sim 1220\text{ cm}^{-1}$ respectively showing the bonding of hydroxylic oxygen atoms to the metal ions. The band at 1525 cm^{-1} (LH_2) and 1520 cm^{-1} ($L'H_2$) can be assigned to $\nu(C-O)$ (phenolic) vibration. In the metal complexes it appears at $\sim 1510\text{ cm}^{-1}$ indicating bonding of phenolic oxygen to the metal ions. In the spectra of Co(II), Ni(II), Cu(II) and Zn(II) complexes, the appearance of a double hump at $\sim 3400\text{ cm}^{-1}$ followed by a sharp peak at $\sim 850\text{ cm}^{-1}$ indicates the presence of coordinated water⁷. In the far IR spectra of the complexes, the bands at $420-460\text{ cm}^{-1}$ and $500-510\text{ cm}^{-1}$ can be assigned to $\nu(M-O)$ and $\nu(M-N)$ vibrations respectively⁸. Thus, the schiff bases behave as bis-bidentate ligands coordinating to the metal ions through both the imine nitrogen and both the phenolic oxygen atoms.

Sub-normal magnetic moments of Co(II) (~ 2.8 B.M.), Ni(II) (~ 2.3 B.M.) and Cu(II) (~ 1.2 B.M.) complexes respectively indicate metal-metal interaction in a polymeric structure.

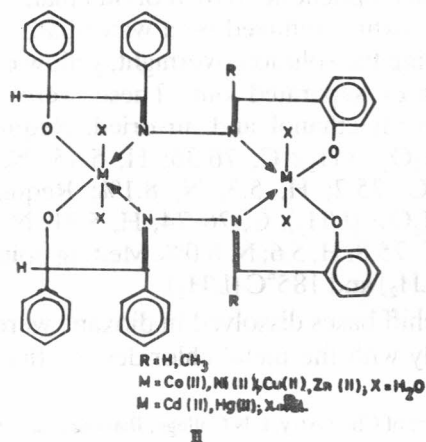
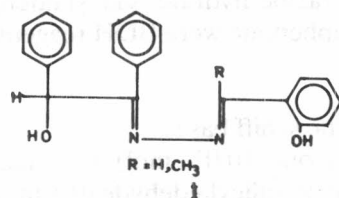
In the electronic spectra of cobalt(II) complexes, four bands are observed at ~ 8350 ($\epsilon = 9$), ~ 16900 ($\epsilon = 18$), ~ 20850 ($\epsilon = 26$) and $\sim 34100\text{ cm}^{-1}$ assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \rightarrow {}^4A_{2g}(F)$, $\rightarrow {}^4T_{1g}(P)$ and charge-transfer respectively. The spectral parameters like D_q , B , ν_2/ν_1 , β_{35} and σ are indicative of an octahedral stereochemistry⁹ (Table 2). In the electronic spectra of nickel(II) complexes three *d-d*

Table 2—Spectral parameters of cobalt(II) and nickel(II) complexes

Compound	D_q (cm^{-1})	B	β_{35}	ν_2/ν_1	σ
$[Co_2L_2 \cdot 4H_2O]$	855	846	0.87	2.02	14.34
$[Co_2L'_2 \cdot 4H_2O]$	866	905	0.93	2.04	75.26
$[Ni_2L_2 \cdot 4H_2O]$	873	1024	0.98	1.88	20.40
$[Ni_2L'_2 \cdot 4H_2O]$	875	942	0.92	1.86	86.95

bands and one CT band are observed at ~ 8730 ($\epsilon = 6.8$) ~ 16450 ($\epsilon = 11.0$), ~ 25100 ($\epsilon = 15.5$) and $\sim 31500\text{ cm}^{-1}$ respectively. The first three bands can be attributed to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $\rightarrow {}^3T_{1g}(F)$ and $\rightarrow {}^3T_{1g}(P)$ transitions, respectively. Calculations of spectral parameters support an octahedral geometry around the nickel(II) ion¹⁰. In the case of copper(II) complexes, the broad absorption band at $\sim 13750\text{ cm}^{-1}$ can be assigned to the transition ${}^2E_g \rightarrow {}^2T_{2g}$. This broadening of *d-d* band may be due to Jahn-Teller effect and a distorted octahedral geometry may be suggested for these two Cu(II) complexes¹¹.

Sub-normal magnetic moments, spectral band positions, high melting points and sparing solubility of the complexes in common organic solvents suggest a polymeric octahedral structure for Co(II) and Ni(II) complexes. The Cu(II) complexes are distorted octahedral, dimeric complexes. The Zn(II) complexes are dinuclear octahedral and a dimeric tetrahedral structure is suggested for the Cd(II) and Hg(II) complexes on the basis of their analytical data, solubility tests and high melting points.



The schiff bases and the metal complexes can be represented by the structures (I) and (II) respectively.

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The reaction of the Schiff base with the metal ions was studied in the presence of various ligands. The results are given in Table I. It is observed that the Schiff base reacts with the metal ions in the presence of ligands to form the metal complexes. The results are given in Table I.

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